268. *The Condensation of Fluorene Derivatives with Acrylonitrile.*

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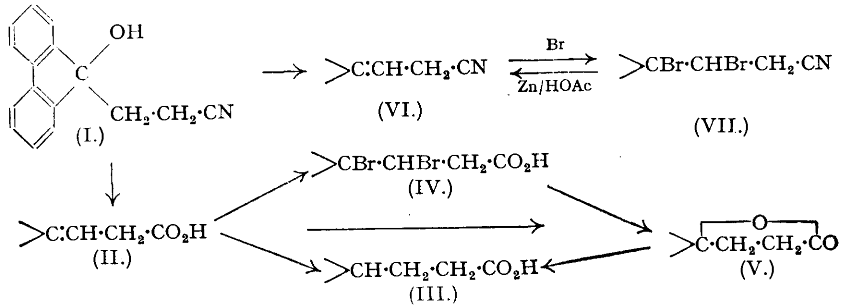
In presence of benzyltrimethylammonium hydroxide, acrylonitrile condenses with 9-phenyl- but not with 9-chloro-, 9-ethyl-, or 9-benzyl-fluorene, or ethyl 9-fluorenylglyoxylate. With 9-fluorenol it yields *β-(9-hydroxy-9-fluorenyl)propionitrile*, the reaction products of which have been studied. Among these is *β-9-fluorenylidenepropionic acid*, which is reduced to β-9-fluorenylpropionic acid from which fluoranthene is synthesised. Cinnamonitrile condenses with fluorene to yield *β-phenyl-β-9-fluorenylpropionitrile*.

In an attempt to insert a single propionic acid residue at the 9-position of the fluorene molecule the action of acrylonitrile on various fluorene derivatives in the presence of benzyltrimethylammonium hydroxide was investigated (cf. Bruson, *J. Amer. Chem. Soc.*, 1942, **64**, 2457, etc.). The failures are recorded above, but 9-phenylfluorene gave β-(9-*phenyl*-9-*fluorenyl)propionitrile*; hydrolysis to the *acid* and cyclisation of the acid chloride gave a product which is probably 4-*keto*-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene*, though formation of a spiran by ring-closure on the phenyl ring is not excluded.

9-Fluorenol reacted rapidly in dioxan with acrylonitrile in presence of the catalyst to form β-(9-*hydroxy*-9-*fluorenyl)propionitrile* (I). This is somewhat unexpected in view of the findings of Bruson and Riener (*J. Amer. Chem. Soc.*, 1943, **65**, 24) that acrylonitrile with alcohols forms cyanoethyl ethers. The nitrile was hydrolysed by sodium hydroxide to β-9-*fluorenylidenepropionic acid* (II), the constitution of which follows from its preparation, catalytic reduction to β-9-fluorenylpropionic acid (III), bromination to a dibromo-acid, presumably 9 : β-*dibromo*-β-9-*fluorenylpropionic acid* (IV), and conversion by sulphuric acid into the *lactone* (V) of β-(9-hydroxy-9-fluorenyl)propionic acid. The lactone was also formed by reduction of the dibromo-acid (IV) with zinc dust and glacial acetic acid, and reduction with hydriodic acid and phosphorus (cf. Rupe and Steinbeck, *Ber.*, 1911, **44**, 584) yielded β-9-fluorenylpropionic acid (III). This acid and the lactone have both been synthesised by other methods (Meyer, *Ber.*, 1913, **46**, 2579; Campbell and Fairfull, this vol. **1102**). All attempts to prepare the hydroxy-acid from the lactone were unsuccessful.



The hydroxy-nitrile (I), when refluxed with hydrochloric acid gave a mixture of β-9-*fluorenylidenepropionitrile* (VI) and the lactone (V), the lactone being obtained in good yield from this unsaturated nitrile by boiling hydrochloric acid or hydrobromic and acetic acids. The nitrile with bromine yielded 9 : β-*dibromo*-β-9-*fluorenylpropionitrile* (VII), whence it was regenerated by zinc and acetic acid.

β-9-Fluorenylpropionic acid was converted by the method of von Braun and Anton (*Ber.*, 1929, **62**, 148) into 1 : 2 : 3 : 4-tetrahydrofluoranthene and thence by chloranil dehydrogenation into fluoranthene.

Cinnamonitrile condensed with fluorene in dioxan or toluene to give β-*phenyl*-β-9-*fluorenylpropionitrile*. Hydrolysis yielded the *acid*, which underwent ring-closure with anhydrous hydrogen fluoride to give an excellent yield of 4-*keto*-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene*.

EXPERIMENTAL.

Chromatographic adsorptions were carried out on alumina (Brockmann). Analyses were by Drs. Weiler and Strauss (Oxford).

Condensation of Fluorenol with Acrylonitrile.—The method of Werner and Grob (*Ber.*, 1904, **37**, 2896) for the preparation of 9-fluorenol gave a product, m. p. 149—152°, lacking the characteristic crystalline appearance of fluorenol when crystallised from benzene and depressing the m. p. of an authentic sample of fluorenol (Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 770). The product is probably the molecular compound of fluorenol and fluorenepinacol obtained by Bachmann (*J. Amer. Chem. Soc.*, 1933, **55**, 1185). Fluorenol, however, was successfully prepared by the following modification. Fluorenone (20 g.) was heated under reflux in ethanol (100 ml.) and concentrated ammonia (100 ml.), and ammonia was passed into the solution. Zinc dust (35 g.) was added in 7-g. portions at 15-minute intervals, heating was continued for a further 30 minutes, and the colourless solution filtered. The filtrate yielded 12 g. of fluorenol, m. p. 150—153° (no m. p. depression with a genuine sample), and gave with water (1 l.) a further 5·5 g. which were crystallised from benzene (m. p. 149—151°).

Acrylonitrile (3 ml.) was added dropwise to a stirred solution of 9-fluorenol (6 g.) and 20% methanolic benzyltrimethylammonium hydroxide solution (1 ml.) so that the temperature was kept at 30—40°. Stirring was continued at room temperature for 3 hours, the solution poured into water (80 ml.), and the yellow oil extracted with ether. The ethereal layer was washed several times with water, dried ($CaCl_2$), and evaporated. The oil (6·6 g.) was dissolved in hot benzene, and light petroleum (b. p. 60—80°) was added. An oily layer formed which deposited crystals of β-(9-*hydroxy*-9-*fluorenyl*)*propionitrile* (1·1 g.), m. p. 105—107° (Found: C, 81·34; H, 5·79; N, 5·89. $C_{10}H_{13}ON$ requires C, 81·66; H, 5·57; N, 5·9%). In another experiment the yellow oil (20·3 g. from 18·2 g. fluorenol) was heated under reflux for 5 hours with sodium hydroxide (8 g.) in water (200 ml.); ammonia was evolved. Dilution with water (200 ml.) gave fluorenol (1·5 g.) and a filtrate which on acidification at 60° with concentrated hydrochloric acid, yielded a semi-solid. This was dried and dissolved in boiling benzene (280 ml.); light petroleum (b. p. 100—120°; 200 ml.) was then added. β-9-*Fluorenylidenepropionic acid* (9·1 g.) separated in colourless elongated prisms, m. p. 136—137° (after further crystallisation from benzene) (Found: C, 80·81; H, 4·85. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%). From the mother-liquors a further 3·6 g., m. p. 129—132°, of the acid were obtained.

The yellow oil (5 g.) was heated under reflux with concentrated hydrochloric acid (150 ml.) and water (150 ml.) for 1½ hours, and the resulting oil extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was extracted with light petroleum (b. p. 100—120°), leaving a brown residue and depositing on cooling β-9-*fluorenylidenepropionitrile* (1·3 g.), which formed colourless needles, m. p. 100—101°, from light petroleum (b. p. 60—80°) (Found: C, 88·36; H, 5·14; N, 6·73. $C_{16}H_{11}N$ requires C, 88·4; H, 5·15; N, 6·45%). The above-mentioned brown residue crystallised from benzene in needles, m. p. 197—199° (1·9 g.), and proved to be the lactone (V) (see below).

Reactions of β-9-*Fluorenylidenepropionitrile*.—Bromine was added to β-9-fluorenylidenepropionitrile (0·5 g.) in acetic acid (3 ml.) at 50° until the brown colour persisted. 9 : β-*Dibromo*-β-9-*fluorenylpropionitrile* separated, was washed with methanol, and crystallised from acetic acid in needles, m. p. 126—127° (yield 0·35 g.) (Found: Br, 42·32. $C_{16}H_{11}NBr_2$ requires Br, 42·4%). When heated under reflux for 30 minutes with zinc dust and acetic acid, it regenerated the unsaturated nitrile. The nitrile (0·2 g.), when boiled under reflux with acetic acid (10 ml.) and hydrobromic acid (10 ml. 34%) for 1 hour, yielded the lactone (V), m. p. 198—200° (0·16 g.). A similar result was obtained with concentrated hydrochloric acid. When the nitrile (0·5 g.) was boiled under reflux with 10% sodium hydroxide (20 ml.), fluorene (0·14 g.), m. p. 111—113°, sublimed. The fluorene was not present as such in the nitrile, since the latter gave no sublimate when water was used.

Reactions of β-9-*Fluorenylidenepropionic Acid*.—Bromine (1·6 g.) was added to the acid (II) (2·4 g.) in acetic acid, and, after 3 hours, water was added. The precipitate was extracted with boiling light petroleum (b. p. 100—120°) which, when cold, yielded 9 : β-*dibromo*-β-9-*fluorenylpropionic acid*, which formed elongated prisms from benzene, m. p. 166—167° (Found: Br, 40·74. $C_{16}H_{12}O_2Br_2$ requires Br, 40·34%). The crude product was boiled under reflux with zinc dust (5 g.) in acetic acid (10 ml.) for 15 minutes; filtration, followed by addition of water, gave the lactone (V), m. p. 198—200° (41% yield after crystallisation from benzene), of β-(9-hydroxy-9-fluorenyl)propionic acid.

The acid (II) (2·4 g.) in acetic acid was reduced with hydrogen (60 lb. pressure) and an Adams platinum catalyst (0·1 g.). When there was no further fall in pressure, air was admitted and the solution shaken. A further addition of the catalyst (0·1 g.) with hydrogen completed the hydrogenation. The volume of the solution was reduced to 10 ml., whereafter water gave an oily precipitate which was extracted several times with light petroleum (b. p. 100—120°) to give β-9-fluorenylpropionic acid, needles (from benzene), m. p. 141—142° (lit., 144°) (Found: C, 80·28; H, 6·25. Calc. for $C_{16}H_{14}O_2$: C, 80·63; H, 5·92%). This acid was also formed by heating the lactone (V) (7·5 g.) with red phosphorus (6 g.), hydriodic acid (*d* 1·9; 25 ml.), and water (10 ml.) for 5 hours under reflux. The mixture was added to water (50 ml.) and extracted with ether. The ethereal layer was washed successively with 1% sodium carbonate, aqueous sodium hydrogen sulphite, and water. The ethereal layer was extracted with sodium carbonate (50 ml. of 60% in 10-ml. portions). Acidification gave a sticky solid, which was extracted five times with 30-ml. portions of light petroleum (b. p. 100—120°) and on cooling yielded β-fluorenylpropionic acid, m. p. 143—144°.

The acid (II) (8 g.) was heated under reflux with 10% sulphuric acid (150 ml.) for 2½ hours, and the mixture poured on ice-water. The *lactone* (V) separated (7·7 g.) and crystallised from benzene in needles, m. p. 200—201°, with a blue fluorescence (Found: C, 80·77; H, 5·0. $C_{16}H_{13}O_2$ requires C, 81·0; H, 5·4%).

Synthesis of Fluoranthene.—β-9-Fluorenylpropionic acid (4·8 g.) was converted into the acid chloride by thionyl chloride and then treated in light petroleum (b. p. 100—120°) with aluminium chloride (von Braun and Anton, *Ber.*, 1929, **62**, 148), thereby giving an oil (3·3 g.) containing 4-keto-1 : 2 : 3 : 4-tetrahydrofluoranthrene [characterised by its 2 : 4-*dinitrophenylhydrazone*, orange crystals (from acetic acid), m. p. 234—236° (Found: N, 13·7. $C_{22}H_{16}O_4N_4$ requires N, 13·96%)]. Chromatographic purification of the oil in benzene on a column, 18″ × 1″, and development with benzene–light petroleum (1 : 1) gave a bright-blue-fluorescing band which separated in the filtrate to give an oil (1·8 g.) and 0·2 g. of yellow prisms (from benzene–light petroleum), m. p. 94—97° (lit., 98°), both of which yielded the dinitrophenylhydrazone described above. On Clemmensen reduction (von Braun *et al.*, *loc. cit.*), followed by chloranil dehydrogenation (Tobler *et al.*, *Helv. Chim. Acta*, 1941, **24**, 100E), the oil gave fluoranthene, m. p. 105—107° (0·06 g.), identified by mixed m. p. and by the picrate.

Condensation of Fluorene and Cinnamonitrile.—Cinnamamide (13 g.) was heated under reflux with thionyl chloride (20 ml.) for 1 hour, the excess of thionyl chloride removed in a vacuum, and the crude cinnamonitrile distilled (b. p. 180—185°/100 mm.), dissolved in ether, and shaken with potassium carbonate solution. Removal of the ether, followed by distillation, gave cinnamonitrile, b. p. 176°/76 mm. (yield, 7 g.; 62%).

Fluorene (5 g.) was heated on the steam-bath for 3½ hours with cinnamonitrile (4·5 g.) and 1 ml. 20% methanolic benzyltrimethylammonium hydroxide in dioxan (35 ml.), and the mixture was poured into water. The resulting solid was boiled with charcoal in ethanol, and water added to the hot filtrate until turbidity occurred. When the mixture cooled, *β-phenyl-β-*9*-fluorenylpropionitrile* separated; it formed prisms, m. p. 151—152° (yield 4·5 g.; 50%), from aqueous ethanol (Found: N, 4·36. $C_{22}H_{17}N$ requires N, 4·75%). The nitrile (9 g.) was boiled under reflux in ethanol (200 ml.) and water (100 ml.) containing sodium hydroxide (15 g.) for 20 hours. The solution, when cold deposited *β-phenyl-β-*9*-fluorenylpropionamide*, needles (from ethanol), m. p. 207—208° (yield 2·7 g.), identical with a sample prepared from the acid chloride and ammonia (Found: N, 4·33. $C_{22}H_{19}ON$ requires N, 4·51%). With concentrated hydrochloric acid the filtrate gave 6·2 g. of *β-phenyl-β-*9*-fluorenylpropionic acid*, m. p. 181—182° after crystallisation from aqueous ethanol (Found: C, 84·28; H, 5·93. $C_{22}H_{18}O_2$ requires C, 84·02; H, 5·9%). The *methyl* ester crystallised from benzene–light petroleum (b. p. 40—60°) (1 : 3) in needles, m. p. 81—82° (Found: C, 83·71; H, 6·4. $C_{23}H_{20}O_2$ requires C, 84·05; H, 6·14%). The acid (1·7 g.) was also obtained by hydrolysing the amide (2 g.) in ethanol (75 ml.) and water (100 ml.) with sodium hydroxide (4 g.) for 30 hours. To the acid (2·5 g.) in a platinum basin, anhydrous hydrogen fluoride (approx. 100 c.c.) was added. After 18 hours the hydrogen fluoride was evaporated, and the residue of 4*-keto-*2*-phenyl-*1 : 2 : 3 : 4*-tetrahydrofluoranthene* triturated with ether and crystallised from glacial acetic acid; prisms, m. p. 162—163° (yield, 90%) (Found: C, 88·80; H, 5·36. $C_{22}H_{16}O$ requires C, 89·12; H, 5·44%).

Condensation of 9*-Phenylfluorene with Acrylonitrile.*—Acrylonitrile (2·5 g.) was added dropwise to a stirred solution of 9-phenylfluorene (5 g.) in dioxan (40 ml.) containing 0·5 ml. of catalyst (see above), the temperature being kept below 35°. After a further 2 hours at room temperature the mixture was poured into water, and the precipitate of *β-phenyl-β-*9*-fluorenylpropionitrile* crystallised from acetic acid or benzene–light petroleum; it formed elongated prisms, m. p. 148—149° (yield, 4·5 g.) (Found: N, 4·36. $C_{22}H_{17}N$ requires N, 4·73%). The nitrile (20 g.) was heated under reflux with sodium hydroxide (30 g.) in ethanol (400 ml.) and water (200 ml.) for 10 hours, and added to ice–water (1500 ml.). The solution was boiled with charcoal, filtered and on acidification yielded *β-phenyl-β-*9*-fluorenylpropionic acid*, plates (from aqueous ethanol), m. p. 159—160° (yield, 20 g.; 90%) (Found: C, 83·57; H, 6·04. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%). The *methyl* ester forms colourless needles (from ethanol), m. p. 97—98° (Found: C, 84·2; H, 6·38. $C_{23}H_{20}O_2$ requires C, 84·2; H, 6·1%). The acid (1·5 g.) was converted into the acid chloride and cyclised in light petroleum with aluminium chloride (see above). Acid was removed from the product with alkali, and the residue (0·72 g.) in benzene adsorbed on a column, 15″ × 1″, and developed with this solvent. The filtrate was collected in 75-ml. portions, one of which yielded an oily solid which after several crystallisations from benzene–light petroleum yielded 4*-keto-*1*-phenyl-*1 : 2 : 3 : 4*-tetrahydrofluoranthene*, m. p. 147—149° (yield, 0·18 g.) (Found: C, 88·4; H, 5·31. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%); the 2 : 4*-dinitrophenylhydrazone* formed orange needles (from acetic acid), m. p. 302—303° (Found: N, 11·7. $C_{28}H_{20}O_4N_4$ requires N, 11·8%).

9*-Alkylfluorenes.*—The alkylfluorenes were prepared from the 9-alkylfluorenols by reduction with hydriodic acid (*d* 1·90) in acetic acid (Wanscheidt and Moldanski, *Ber.*, 1931, **64**, 917) but, contrary to statements by these authors, we were unable thus to reduce 9-methylfluorenol, m. p. 172—173° (lit., 173°) (Found: C, 85·39; H, 6·13. Calc. for $C_{14}H_{12}O$: C, 85·63; H, 6·16%), the product isolated having a m. p. much higher than that of 9-methylfluorene. 9-Benzylfluorenol gave an 85% yield of 9-benzylfluorene, m. p. 131—133° (lit., 133°) (Found: C, 93·73; H, 6·61. Calc. for $C_{20}H_{16}$: C, 93·74; H, 6·26%).

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